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## (54) LITHIUM SECONDARY BATTERY

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a positive electrode material for non-aqueous electrolyte secondary batteries which makes charge/discharge electricity in a high rate possible, has high capacity, has excellent durability in charge/discharge- electricity cycle, and has high safety.

**SOLUTION:** In the lithium secondary battery equipped with the positive electrode active material layer which has a lithium transition metal complex oxide as a principal component, the above lithium transition metal complex oxide is constituted of a mixture with a lithium-nickel-manganese-M complex having R-3m rhomb structure expressed by  $LixNiyMn1-y-zMzO2$  (however, x is  $0.9 \leq x \leq 1.2$ , y is  $0.40 \leq y \leq 0.60$ , and z is  $0 \leq z \leq 0.2$ , and M is chosen from either of Fe, Co, Cr, or Al), and a lithium-manganese spinel complex oxide having a Fd-3m spinel structure and expressed with  $LipMn2O4$  (however, p is  $1 \leq p \leq 1.3$ ).

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the lithium secondary battery provided with the improved positive active material layer.

#### [0002]

[Description of the Prior Art] In recent years, the expectation for small size and the nonaqueous electrolyte secondary battery which is lightweight and has high energy density is growing as portableizing of apparatus and cordless making progress. The multiple oxide of lithium, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiMnO}_2$ , and a transition metal is known by the active material for nonaqueous electrolyte secondary batteries.

[0003] Research of the multiple oxide of lithium and manganese is briskly done in it as a cheap material whose safety is especially high these days. These are used for positive active material and development of the nonaqueous electrolyte secondary battery of the high tension by combining negative electrode active material, such as occlusion and a carbon material which can be emitted, and high energy density is furthered in lithium.

[0004] Generally, the positive active material used for a nonaqueous electrolyte secondary battery becomes lithium which is main active material from the multiple oxide which made transition metals including cobalt, nickel, and manganese dissolve. With kinds of the transition metal used, electrode characteristics, such as electric capacity, reversibility, operating potential, and safety, change. For example, the nonaqueous electrolyte secondary battery which used for positive active material the R-3-m rhombohedron halite laminar multiple oxide which made cobalt and nickel dissolve like  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ , While being able to attain 140 - 160 mAh/g and 180 - 200 mAh/g, and comparatively high capacity density, respectively, high voltage regions, such as 2.5-4.3V, show good reversibility.

#### [0005]

[Problem(s) to be Solved by the Invention] However, when a cell is warmed, since the problem on

which a cell generates heat easily by the reaction of the positive active material at the time of charge and an electrolysis solution solvent, cobalt used as a raw material, and nickel are expensive, there is a problem to which the cost of an active material becomes high.

[0006]The nonaqueous electrolyte secondary battery which used for the active material the spinel type multiple oxide which consists of  $\text{LiMn}_2\text{O}_4$  which uses on the other hand comparatively cheap manganese as a raw material, Although a cell does not generate heat comparatively easily due to the reaction of the positive active material at the time of charge, and an electrolysis solution solvent, SUBJECT that capacity is as low as 100 - 120 mAh/g compared with an above-mentioned cobalt system and nickel series active material, and charge-and-discharge cycle durability is scarce occurs.

[0007]Instead of using these independent lithium transition metal multiple oxides as positive active material,  $\text{LiMnO}_2$  of an ortho rhombic system, Mixing at least a kind of lithium transition metal multiple oxide chosen from the group which consists of  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ , and  $\text{LiMn}_2\text{O}_4$  is proposed by JP,H9-180718,A. The cell using this mixture originates in  $\text{LiMnO}_2$ , and there is a problem which runs short of charge-and-discharge cycle durability.  $\text{LiMnO}_2$  also has the problem that the charge-and-discharge capacity in a high rate is low.

[0008]The lithium secondary battery which consists of a three-sort mixture of  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , and  $\text{LiCoO}_2$  is proposed by JP,H11-3698,A. The cell using the three-sort mixture of this  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , and  $\text{LiCoO}_2$  originates in use of  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$ , and there is a problem which is not enough.

[0009]Were made in order that this invention might solve such SUBJECT, and the purpose, The charge and discharge in a high rate are possible, capacity is high, and it is in providing the nonaqueous electrolyte secondary battery with sufficient high energy density and high-electric-current discharge characteristic using the high safety positive electrode material for nonaqueous electrolyte secondary batteries excellent in charge-and-discharge cycle durability.

[0010]

[Means for Solving the Problem]In a lithium secondary battery provided with a positive active material layer where this invention uses a lithium transition metal multiple oxide as the main ingredients in order to attain the above-mentioned purpose, The above-mentioned lithium transition metal multiple oxide  $\text{Li}_x\text{Ni}_y\text{Mn}_{1-y-z}\text{M}_z\text{O}_2$  (however, as for x,  $0.40 \leq y \leq 0.60$  and z of  $0.9 \leq x \leq 1.2$  and y are  $0 \leq z \leq 0.2$ , and M is chosen from Fe, Co, Cr, or Al atoms.) -- with a lithium nickel manganese M multiple oxide expressed. It has  $\text{Fd}3\text{m}$  Spinel structure and is characterized by consisting of a mixture with a lithium manganese spinel multiple oxide expressed with  $\text{Li}_p\text{Mn}_2\text{O}_4$  (however, p is  $1 \leq p \leq 1.3$ ).

[0011]As for the above-mentioned lithium nickel manganese M multiple oxide, in this invention, it is preferred that it is  $\text{R}3\text{-m}$  rhombohedron structure. Since it becomes difficult to take a stable  $\text{R}-3\text{-m}$  rhombohedron structure with y being less than 0.40, it is not desirable. Since safety will fall if y exceeds 0.60, it is not desirable. As for y, 0.45-0.55 are adopted especially preferably. As for x,  $0.9 \leq x \leq 1.2$  is adopted for a capacity manifestation.

[0012]Improvement in charge-and-discharge cycle durability, safety, capacity, etc. can be aimed at by adding one atom of Fe, Co, Cr, and aluminum further to the above-mentioned lithium nickel manganese M multiple oxide. the additions z of M atom are 0-0.2 – desirable – 0.01 to 0.18 – it is 0.05-0.16 especially preferably.

[0013]Although another above-mentioned lithium multiple oxide used by this invention is a lithium manganese spinel multiple oxide which has  $Fd3m$  Spinel structure and is expressed with  $Li_pMn_2O_4$  (however, p is  $1 < p <= 1.3$ ), having alkali earth metal elements and transition metal elements other than manganese for a manganese element in this manganese spinel – 2-10-mol % – charge-and-discharge cycle durability can be raised by replacing. Magnesium, aluminum, iron, and chromium are chosen as a desirable substituted element of manganese in a manganese spinel.

[0014]As for content of the above-mentioned lithium nickel manganese M multiple oxide in the above-mentioned mixture, in this invention, it is preferred that it is 30 to 70 % of the weight. Since capacity of a lithium cell falls that the above-mentioned content is less than 30 % of the weight or charge-and-discharge cycle durability falls, it is not desirable. Since service capacity in a high rate will fall or discharge average voltage will fall if the above-mentioned content exceeds 70 % of the weight, it is not desirable. Especially the desirable above-mentioned content is 40 to 60 % of the weight.

[0015]In this invention, it is preferred that granular material press density when press restoration only of the powder is carried out by a pressure of  $1 t/cm^2$  the mixed powder end of the above-mentioned multiple oxide is more than  $2.7 g/cm^3$ . According to this, a mixture is made with a slurry, and coating and desiccation, and when it presses, capacity per volume can be made high at charge collector aluminum foil. Especially desirable granular material press density is more than  $2.9 g/cm^3$ . Granular material press density more than  $2.7 g/cm^3$  is attained by rationalizing particle size distribution of a mixed powder object. That is, particle size distribution has width, a volume fraction of few particle diameter is 20 to 50%, and densification can be attained by narrowing particle size distribution of a large diameter etc.

[0016]If a mixture of this invention is used, from a case where each independent lithium transition metal multiple oxide used for mixing is used, charge and discharge in a high rate are possible, and capacity and battery capacity whose balance of safety improved can be revealed. Outstanding battery capacity of capacity, safety, and charge-and-discharge cycle stability can be obtained from a case where the same positive active material as a transition metal element content which consisted of an independent lithium transition metal compound, and was used for mixing is used. Although a cause by which this physical mixture is superior to an independent substance is not clear, Since a lithium nickel manganese M multiple oxide (nickel/Mn=0.6 / 0.4 – 0.4/0.6) has specially high safety and the manifestation nature of capacity is comparatively good, it is thought that a synergistic effect was revealed by mixing.

[0017]

[Embodiment of the Invention]The crystal structure used for this invention as a process of  $Li_xNi_yMn_{1-x-y}$

$y-z M_z O_2$  (lithium nickel manganese M multiple oxide) which consists of R-3 m of rhombohedron, For example, 500-'s1000 \*\* of solid phase techniques calcinating the mixture of a manganese compound, a lithium compound, and a nickel compound under an inert gas atmosphere or in the atmosphere and the fused salt method in 500-850 \*\* are mentioned.

[0018]The lithium nickel manganese M multiple oxide in which the crystal structure used for this invention consists of rhombohedron stratified rock salt type structure, For example, the thing for which 500-1000 \*\* of solid phase techniques calcinate the mixture of the multiple oxide or compound hydroxide which consists of a nickel manganese metallic element, a manganese compound, and a lithium compound under oxygen gas content atmosphere, It can obtain by the fused salt method which adds a nickel manganese metallic element M content compound in 500-850 \*\* lithium content fused salt.

[0019]As a nickel source raw material, oxides (NiO etc.), hydroxide (NiOH), oxy hydroxide (NiOOH), etc. are mentioned. As a manganese source raw material, oxides ( $Mn_2O_3$ ,  $MnO$ ,  $MnO_2$ , etc.), the hydrate of these oxides, oxy hydroxide, etc. are mentioned. As a manganese source raw material, the compound of trivalent manganese is more preferred. These manganese source raw materials may be used alone, and may use two or more sorts together.

[0020]As a source raw material of the metallic element (M), simple substance metal, hydroxide, an oxide, oxy hydroxide, a chloride, a nitrate, etc. are used. The source raw material of these metallic elements (M) may be used alone, and may use two or more sorts together.

[0021]Positive electrode mixture is formed by mixing a carbon system conducting material and binding material, such as acetylene black, black lead, and Ketchen black, to the powder of the mixture of this invention. Polyvinylidene fluoride, polytetrafluoroethylene, polyamide, carboxymethyl cellulose, an acrylic resin, etc. are used for binding material. the slurry which consists of the solvent or carrier fluid of the powder of the mixture of this invention, a conducting material, binding material, and binding material -- positive pole collectors, such as aluminium foil, -- coating - it dries and rolls [ press ] and a positive active material layer is formed on a positive pole collector.

[0022]In the lithium cell of this invention, carbonic ester is preferred as a solvent of an electrolytic solution. Carbonic ester can use both annular and a chain. Propylene carbonate, ethylene carbonate, etc. are illustrated as cyclic carbonate. As chain carbonic ester, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, methylpropyl carbonate, methyliso propyl carbonate, etc. are illustrated.

[0023]In this invention, it is independent in the above-mentioned carbonic ester, or two or more sorts can be mixed and used. It may be used mixing with other solvents. If chain carbonic ester and cyclic carbonate are used together depending on the material of negative electrode active material, a discharge characteristic, cycle durability, and charge and discharge efficiency may be improvable. It is good also as a gel-polymer-electrolyte by adding a fluoridation vinylidene-hexafluoropropylene copolymer (for example, Atochem Kiner) and a fluoridation vinylidene-perfluoro propylvinyl ether copolymer to these organic solvents, and adding the following solute.

[0024]As a solute,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ , It is preferred to use any one or more sorts of the lithium salt which uses  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{CF}_3\text{CO}_2^-$ ,  $(\text{CF}_3\text{SO}_2^-)_2$  N-, etc. as an anion. As for an above-mentioned electrolytic solution or polymer electrolyte, it is preferred to add the electrolyte which consists of lithium salt by the concentration of 0.2 - 2.0 mol/l to the above-mentioned solvent or solvent content polymer. If it deviates from this range, ionic conductivity will fall and electrolytic electrical conductivity will fall. 0.5 - 1.5 mol/l is selected more preferably. Porous polyethylene and a porous polypropylene film are used for a separator.

[0025]The negative electrode active material in this invention is the material which emits [ occlusion and ] a lithium ion. Although the material in particular that forms such negative electrode active material is not limited, an oxide, carbon compounds, a silicon carbide compound, a silicon oxide compound, a titanium sulfide, a boron carbide compound, etc. which made the subject the metal of a lithium metal, a lithium alloy, a carbon material, the periodic table 14, and 15 fellows, for example are mentioned.

[0026]As a carbon material, what carried out the pyrolysis of the organic matter on various pyrolysis conditions, an artificial graphite, natural graphite, soil black lead, expanded graphite, scaly graphite, etc. can be used. The compound which makes the tin oxide a subject can be used as an oxide. Copper foil, nickel foil, etc. are used as a negative pole collector.

[0027]As for the anode and negative electrode in this invention, it is preferred to knead an active material with an organic solvent, to consider it as slurry, and to obtain this slurry by applying, drying and pressing it in it to a metal foil collector. There are no restrictions in particular in the shape of the lithium cell of this invention. A sheet shaped (what is called film state), the letter of folding, a wound type closed-end cylindrical shape, a button form, etc. are chosen according to a use.

[0028]

[Example]Next, although this invention is explained about concrete working example 1-8 and the comparative examples 1-4, this invention is not limited to these working example.

[0029]<<Working example 1>> An ammonia solution and sodium hydroxide solution were made to add and coprecipitate in nickel sulfate and a manganese sulfate (mole ratio 1:1) mixed water solution, and nickel manganese coprecipitation hydroxide (nickel: manganese-atoms ratio =1:1) was obtained by heating and desiccation at 150 \*\*. This nickel manganese coprecipitation hydroxide was calcinated and ground in the atmosphere at 550 \*\*, and nickel manganic acid ghost powder was obtained. These nickel manganic acid ghost powder and lithium carbonate powders were mixed, it calcinated and ground in a nitrogen gas atmosphere at 800 \*\*, and  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  with a mean particle diameter of 4 micrometers was compounded. X-ray diffraction analysis by CuKalpah of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure. Dry blending of electrolytic manganese dioxide powder and the lithium carbonate powders was carried out, 800 \*\* was calcinated in the atmosphere for 15 hours, grinding and classification of were done, and  $\text{Li}_{1.05}\text{Mn}_{2}\text{O}_4$  powder

with a mean particle diameter of 7 micrometers was obtained. X-ray diffraction analysis by CuKalpah of this powder showed that it was Fd3m Spinel structure.  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and  $\text{Li}_{1.05}\text{Mn}_{2}\text{O}_4$  are mixed

at a rate of 50:50 by a weight ratio, It was 2.90 g/cm<sup>3</sup>, when the hydraulic press of this end of mixed powder was carried out by the pressure of 1 t/cm<sup>2</sup> and granular material press density was calculated from volume and weight. N-methyl-pyrrolidone \*\*\*\*\* ball mill mixing of this end of mixed powder, acetylene black, and polyvinylidene fluoride was carried out by the weight ratio of 83/10/7, and it was considered as the slurry. This slurry was applied on the 20-micro-thick aluminium foil positive pole collector, it dried at 150 \*\*, and N-methyl pyrrolidone was removed. Roll press rolling was carried out to after an appropriate time, and the positive electrode body was obtained. 300-micro-thick metal lithium foil is used for a separator at a negative electrode using 25-micro-thick porous polyethylene, nickel foil is used for a negative pole collector, 1M LiPF<sub>6</sub>/EC+DEC (1:1) is used for an electrolysis solution, and it is \*\*\*\*\* within an argon glove box about coin cell 2030 type. And it charges with the final voltage 4.3V at 1 mA under a 25 \*\* temperature atmosphere, While discharging to 3.0V by 5 mA (discharge rate 1C) of constant current and investigating a high-electric-current discharge characteristic, It charged with the final voltage 4.3V at 1 mA, the charge-and-discharge cycle test discharged to 3.0V by 1 mA (discharge rate 0.2C) of constant current was done 20 times, and the capacity maintenance rate was searched for from the ratio of the initial service capacity after 2 times charge and discharge, and the service capacity after 20 times charge and discharge. For battery safety evaluation, the cell after 4.3V charge was disassembled and it asked for exothermic starting temperature when putting the anode into the well-closed container and carrying out temperature up to a sample using nothing and a differential-scanning-calorimetry device with an electrolysis solution solvent. As a result, as for 124 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 227 \*\* in exothermic starting temperature 93% 92%.

[0030]<<Working example 2>> LiNi<sub>0.6</sub>Mn<sub>0.4</sub>O<sub>2</sub> which set nickel of a lithium nickel manganese multiple oxide, and the atomic ratio of manganese to 0.60:0.40, Li<sub>1.05</sub>Mn<sub>2</sub>O<sub>4</sub> was mixed at a rate of 50:50 by the weight ratio, and also the positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 130 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 221 \*\* in exothermic starting temperature 94% 92%.

[0031]<<Working example 3>> Nickel of a lithium nickel manganese multiple oxide, and LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> whose atomic ratio of manganese is 0.50:0.50, Li<sub>1.05</sub>Mn<sub>2</sub>O<sub>4</sub> was mixed at a rate of 40:60 by the weight ratio, and also the positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 122 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 220 \*\* in exothermic starting temperature 94% 93%.

[0032]<<Working example 4>> LiNi<sub>0.55</sub>Mn<sub>0.45</sub>O<sub>2</sub> which set nickel of a lithium nickel manganese multiple oxide, and the atomic ratio of manganese to 0.55:0.45, Li<sub>1.05</sub>Mn<sub>2</sub>O<sub>4</sub> was mixed at a rate of 30:70 by the weight ratio, and also the positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 121 mAh/g,

and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 220 \*\* in exothermic starting temperature 94% 94%.

[0033]<<Working example 5>> It replaces with nickel sulfate and the manganese sulfate (mole ratio 1:1) mixed water solution of above-mentioned working example 1, Nickel sulfate, manganese sulfate, and a cobalt sulfate (mole ratio 9:9:2) mixed water solution were used, and also

$\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1}\text{O}_2$  with a mean particle diameter of 5 micrometers was compounded as positive active material like above-mentioned working example 1. X-ray diffraction analysis by CuKalpah of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure.

$\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1}\text{O}_2$ , When  $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$  was mixed at a rate of 50:50 by the weight ratio, the hydraulic press of this end of mixed powder was carried out by the pressure of  $1 \text{ t/cm}^2$  and granular material press density was calculated from volume and weight, it was  $2.95\text{g}/\text{cm}^3$ . The positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 128 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 226 \*\* in exothermic starting temperature 95% 93%.

[0034]<<Working example 6>> It replaces with nickel sulfate and the manganese sulfate (mole ratio 1:1) mixed water solution of above-mentioned working example 1, Nickel sulfate, manganese sulfate, and a chromium-sulfate (mole ratio 9:9:2) mixed water solution were used, and also

$\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Cr}_{0.1}\text{O}_2$  with a mean particle diameter of 5 micrometers was compounded as positive active material like above-mentioned working example 1. X-ray diffraction analysis by CuKalpah of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure.

$\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Cr}_{0.1}\text{O}_2$ , When  $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$  was mixed at a rate of 50:50 by the weight ratio, the hydraulic press of this end of mixed powder was carried out by the pressure of  $1 \text{ t/cm}^2$  and granular material press density was calculated from volume and weight, it was  $2.92\text{g}/\text{cm}^3$ . The positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 126 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 230 \*\* in exothermic starting temperature 95% 93%.

[0035]<<Working example 7>> It replaces with nickel sulfate and the manganese sulfate (mole ratio 1:1) mixed water solution of above-mentioned working example 1, Nickel sulfate, manganese sulfate, and a ferrous sulfate (mole ratio 9:9:2) mixed water solution were used, and also

$\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Fe}_{0.1}\text{O}_2$  with a mean particle diameter of 5 micrometers was compounded as positive active material like above-mentioned working example 1. X-ray diffraction analysis by CuKalpah of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure.

$\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Fe}_{0.1}\text{O}_2$ , When  $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$  was mixed at a rate of 50:50 by the weight ratio, the hydraulic press of this end of mixed powder was carried out by the pressure of  $1 \text{ t/cm}^2$  and granular material press density was calculated from volume and weight, it was  $2.90\text{g}/\text{cm}^3$ . The positive electrode body and the cell were produced like above-mentioned working example 1, and the

characteristic was evaluated. As a result, as for 123 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 231 \*\* in exothermic starting temperature 94% 93%. [0036]<Working example 8> It replaces with nickel sulfate and the manganese sulfate (mole ratio 1:1) mixed water solution of above-mentioned working example 1, Nickel sulfate, manganese sulfate, and an aluminum sulfate (mole ratio 9:9:2) mixed water solution were used, and also

$\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{aluminum}_{0.1}\text{O}_2$  with a mean particle diameter of 5 micrometers was compounded as positive active material like above-mentioned working example 1. X-ray diffraction analysis by CuKalp of this powder showed that it was R-3-m rhombohedron stratified rock salt type structure.  $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{aluminum}_{0.1}\text{O}_2$ , When  $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$  was mixed at a rate of 50:50 by the weight ratio, the hydraulic press of this end of mixed powder was carried out by the pressure of 1 t/cm<sup>2</sup> and granular material press density was calculated from volume and weight, it was 2.87g/[cm ]<sup>3</sup>. The positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 124 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 233 \*\* in exothermic starting temperature 94% 93%. [0037]<Comparative example 1>  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  used in above-mentioned working example 1 was used alone, and also the positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 128 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 230 \*\* in exothermic starting temperature 92% 85%.

[0038]<Comparative example 2> An ammonia solution and sodium hydroxide solution were made to add and coprecipitate in nickel sulfate and a manganese sulfate (mole ratio 0.70:0.30) mixed water solution, and nickel manganese coprecipitation hydroxide (nickel: manganese-atoms ratio =0.70:0.30) was obtained by heating and desiccation at 150 \*\*. This nickel manganese coprecipitation hydroxide was calcinated and ground in the atmosphere at 550 \*\*, and nickel manganic acid ghost powder was obtained. This nickel manganic acid ghost powder and lithium hydroxide powder were mixed, and it calcinated at 480 \*\*, it calcinated and ground at 800 \*\* in the atmosphere further, and  $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$  was compounded. This  $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$  was used alone, and also the positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 167 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 200 \*\* in exothermic starting temperature 91% 86%.

[0039]<Comparative example 3>  $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$  used in above-mentioned working example 1 was used alone, and also the positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 117 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 220 \*\* in exothermic starting temperature 93% 94%.

[0040]<Comparative example 4> An ammonia solution and sodium hydroxide solution were made to add and coprecipitate in nickel sulfate and a manganese sulfate (mole ratio 0.25:0.75) mixed water

solution, and nickel manganese coprecipitation hydroxide (nickel: manganese-atoms ratio =0.25:0.75) was obtained by heating and desiccation at 150 \*\*. This nickel manganese coprecipitation hydroxide was calcinated and ground in the atmosphere at 550 \*\*, and nickel manganic acid ghost powder was obtained. This nickel manganic acid ghost powder and lithium hydroxide powder were mixed, and it calcinated at 480 \*\*, it calcinated and ground at 800 \*\* in a nitrogen atmosphere further, and  $\text{LiNi}_{0.25}\text{Mn}_{0.75}\text{O}_2$  was compounded. This  $\text{LiNi}_{0.25}\text{Mn}_{0.75}\text{O}_2$  was used alone, and also the positive electrode body and the cell were produced like above-mentioned working example 1, and the characteristic was evaluated. As a result, as for 119 mAh/g, and 1C capacity / 0.2C capacity, the capacity maintenance rate was [ initial capacity ] 230 \*\* in exothermic starting temperature 87% 83%. [0041]As reference, the multiple oxide and evaluation result which were used by above-mentioned working example 1-8 and the comparative examples 1-4 are collectively shown in the following table. [Table 1]

	第 1 活 物 質 (%)	第 2 活 物 質 (%)	混合比 (%)	容 量 (mA h/g)	IC 容量 (%)	容量保持率 (%)	充電開始溫度 (°C)
実施例 1	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> O <sub>2</sub>	5.0	Li <sub>1-x</sub> Mn <sub>x</sub> O <sub>2</sub>	5.0	1.24	9.2	9.3
実施例 2	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> O <sub>2</sub>	5.0	Li <sub>1-x</sub> Mn <sub>x</sub> O <sub>2</sub>	5.0	1.30	9.2	9.4
実施例 3	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> O <sub>2</sub>	4.0	Li <sub>1-x</sub> Mn <sub>x</sub> O <sub>2</sub>	6.0	1.22	9.3	9.4
実施例 4	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> O <sub>2</sub>	3.0	Li <sub>1-x</sub> Mn <sub>x</sub> O <sub>2</sub>	7.0	1.21	9.4	9.4
実施例 5	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> Co <sub>0.1</sub> O <sub>2</sub>	5.0	Li <sub>1-x</sub> Mn <sub>x</sub> O <sub>2</sub>	5.0	1.28	9.3	9.5
実施例 6	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> Cr <sub>0.1</sub> O <sub>2</sub>	5.0	Li <sub>1-x</sub> Mn <sub>x</sub> O <sub>2</sub>	5.0	1.26	9.3	9.5
実施例 7	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> Fe <sub>0.1</sub> O <sub>2</sub>	5.0	Li <sub>1-x</sub> Mn <sub>x</sub> O <sub>2</sub>	5.0	1.23	9.3	9.4
実施例 8	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> Al <sub>0.1</sub> O <sub>2</sub>	5.0	Li <sub>1-x</sub> Mn <sub>x</sub> O <sub>2</sub>	5.0	1.24	9.3	9.4
比較例 1	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> O <sub>2</sub>	1.00	—	—	1.28	8.5	9.2
比較例 2	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> O <sub>2</sub>	1.00	—	—	1.67	8.6	9.1
比較例 3	—	—	Li <sub>1-x</sub> Mn <sub>x</sub> O <sub>2</sub>	1.00	1.17	9.4	9.3
比較例 4	LiNi <sub>0.8</sub> Mn <sub>0.12</sub> O <sub>2</sub>	1.00	—	—	1.19	8.3	8.7

[0042]

[Effect of the Invention] In the lithium secondary battery provided with the positive active material layer which uses a lithium transition metal multiple oxide as the main ingredients as explained above, By

using the mixture of the multiple oxide of this invention for a lithium transition metal multiple oxide, the charge and discharge in a high rate are possible, and capacity and the battery capacity whose balance of safety improved can be revealed from the case where each independent lithium transition metal multiple oxide used for mixing is used.

[0043]The outstanding battery capacity of capacity, safety, and charge-and-discharge cycle stability can be obtained from the case where the same positive active material as the transition metal element content which consisted of an independent lithium transition metal compound, and was used for mixing is used.

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[Translation done.]